

Stable High Conductivity Bilayered Electrolytes For Low-Temperature Solid Oxide Fuel Cells

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Objectives

- Develop a stable, high-conductivity bilayer electrolyte for low temperature SOFCs.
- Develop suitable high-performance electrodes compatible with the electrolyte.
- Benchmark the performance of the electrolyte.
- Model the performance of the electrolyte.
- Optimize the thickness ratio of the constituent layers of the bilayer electrolyte for maximum conductivity and stability of the bilayer.

Key Milestones

- Demonstrated that the bilayer concept works, resulting in a high-conductivity low-temperature electrolyte.
- Discovered a new oxide ion conductor, $\text{Bi}_{1.88}\text{Dy}_{0.08}\text{W}_{0.04}\text{O}_3$, with the highest conductivity of any known electrolyte.
- Developed a colloidal deposition technique for fabrication of thin bilayer electrolytes.
- Derived a continuum-level electrochemical model of defect transport in SOFCs.
- Deployed the transport model to optimize thickness ratio of constituent layers of the bilayer.

Approach

Solid oxide fuel cells (SOFCs) offer great promise for clean and efficient conversion of chemical energy to electricity while providing significant environmental benefits. They produce negligible hydrocarbons, CO , NO_x and about one-third less CO_2 per kilowatt-hour than internal combustion engines. Alas, current technology uses a yttria-stabilized zirconia (YSZ) electrolyte, which operates in the region of 1000°C to avoid unacceptably high ohmic losses. Such high temperatures demand (a) specialized (expensive) materials for interconnects and insulation, (b) time to heat up to the operating temperature, and (c) energy input to arrive at the operating temperature. Thus, if SOFCs could be designed to give a reasonable power output at low ($< 600^\circ\text{C}$) to intermediate temperatures ($600 - 800^\circ\text{C}$), tremendous benefits may be accrued. At low temperatures, it becomes feasible to use ferritic steel for interconnects instead of expensive and brittle ceramic materials, such as LaCrO_3 and its derivatives. Also, sealing becomes easier and more reliable, rapid start-up is facilitated, thermal stresses (e.g., those caused by thermal expansion mismatches) are reduced, radiative losses ($\sim T^4$) become minimal, electrode sintering becomes negligible, and (due to a smaller thermodynamic penalty) the SOFC operating cycle would be more efficient. Combined, these improvements result in reduced initial and operating costs. However, at lower temperatures, the conductivity of the conventional YSZ electrolyte decreases to the point where it cannot supply electrical current efficiently to an external load.

In light of this, we are developing a bilayer electrolyte, shown in Figure 1, comprised of erbia-stabilized bismuth oxide (ESB) on the air side, and samaria- or gadolinia-doped ceria (SDC or GDC) on the fuel side. Bismuth oxide and doped ceria are among the highest ionic conducting electrolytes. Moreover, bismuth oxide-based electrolytes are the only known solid oxide electrolytes to have an ionic conductivity sufficient for low temperature operation [1]. The problem is that in reducing conditions, ceria becomes a mixed conductor

and bismuth oxide decomposes. In the bilayer arrangement shown in Figure 1, however, the ceria layer protects the bismuth oxide layer from decomposing by shielding it from very low P_{O_2} s and the ESB layer blocks electronic flux through the electrolyte. Therefore, at worst, an SDC\ESB bilayer should have the high conductivity of SDC, but with improved efficiency due to the electronic flux barrier provided by ESB. At best, the conductivity of the bilayer should approach that of ESB with a sufficiently thin layer of SDC. Further, solid solutions at the SDC-ESB interface, if present, are not detrimental to the bilayer's performance as ceria-bismuth oxide solid solutions have conductivities comparable to the host lattice [2, 3].

A primary issue concerning SDC\ESB bilayers is assessing the stability of ESB in this arrangement for

various fuel cell operating conditions, which, as shown in Figure 1, is a function of the relative thicknesses of the layers. Therefore, it is necessary to optimize the relative thickness of the SDC and ESB layers to achieve the disparate goals of high conductance of the bilayer electrolyte and adequate stability. To achieve this goal it is required that: (a) the oxygen partial pressure, P_{O_2} , at the SDC-ESB interface is high enough ($> \sim 10^{-14}$ atm.) in *open-circuit* conditions, and/or (b) the voltage drop across the ESB layer is low enough ($< \sim 0.6$ V at 500 °C) in *closed-circuit* conditions to prevent decomposition of the ESB layer. To further our fundamental understanding of this, we have combined modeling with experimentation in the search for an optimal thickness ratio. These electrochemical models predict the performance of bilayer (and single layer) electrolytes as a function of operating conditions and thickness ratio.

BILAYER CONCEPT

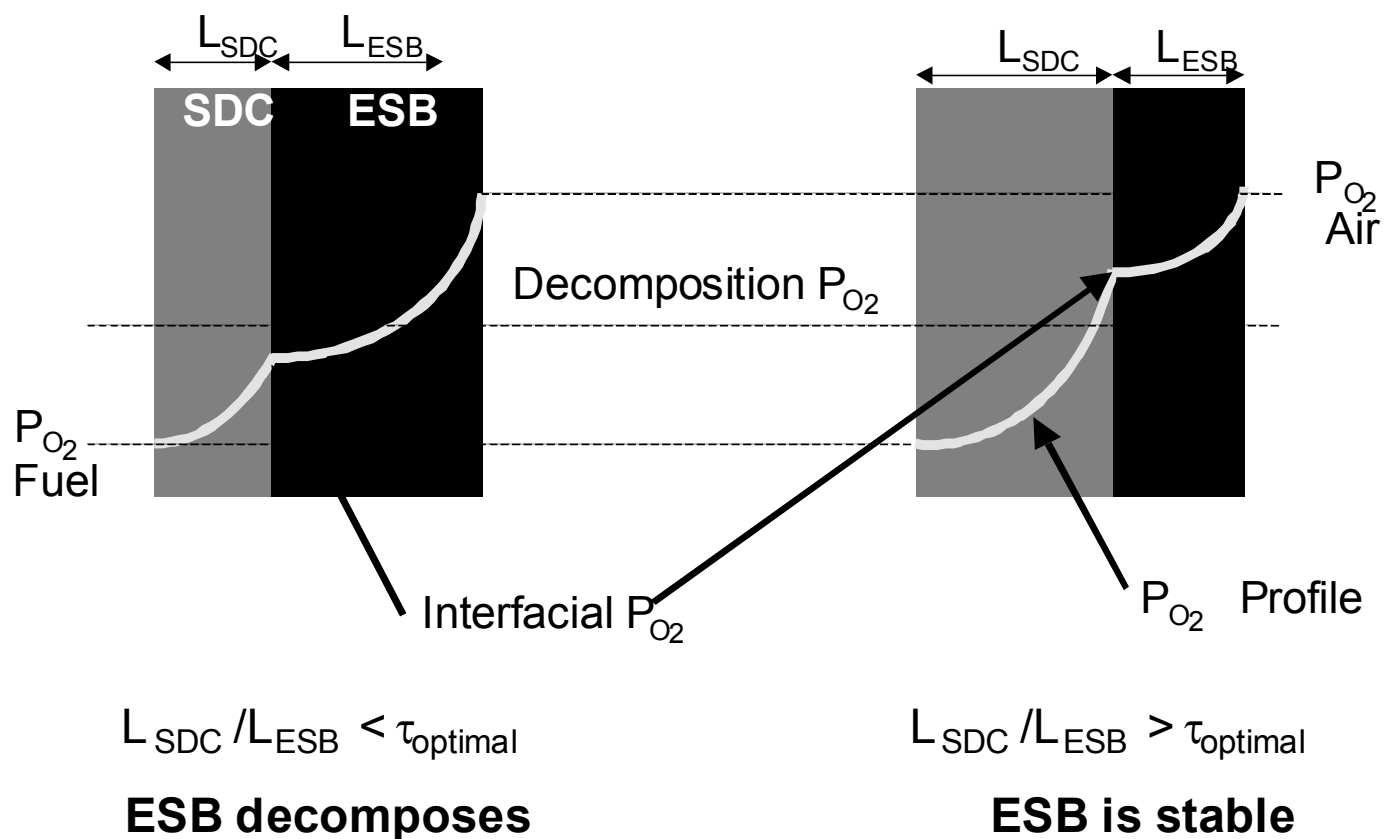


Figure 1. Conceptual representation of a bilayered electrolyte showing the effect of the thickness ratio on interfacial P_{O_2} relative to the decomposition P_{O_2}

Results

In this brief summary, we first report on the experimental validation of the bilayer concept. Figure 2 shows the variation of the cells *open-circuit* potential (OCP) and transference number, t_i , with thickness ratio ($L_{\text{ESB}}/L_{\text{SDC}}$). The results clearly validate the bilayer concept, showing that an increase in the relative thickness of the ESB layer increases the cell's OCP and t_i . We expect even higher OCP and t_i values with thicker ESB and optimized electrodes in the near future.

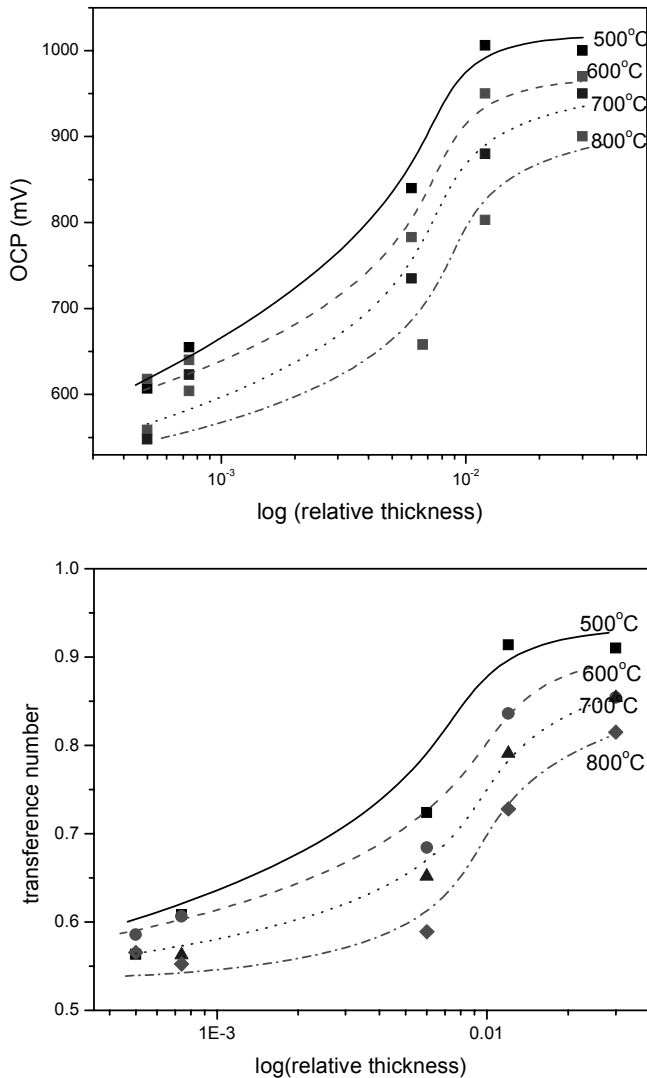


Figure 2. Effect of relative thickness ($L_{\text{ESB}}/L_{\text{SDC}}$) on (a) OCP and (b) t_i relation of bilayer electrolyte SOFC with air at the cathode (Au) and $\text{H}_2/\text{H}_2\text{O}$ at the anode (Pt).

The primary issue for SDC\ESB bilayers is assessing the stability of ESB in this arrangement for various fuel cell operating conditions and optimizing the relative thickness of the SDC and ESB layers so that the chemical or electrical potential difference across the ESB layer is always below the decomposition potential of ESB. The performance and stability models that were developed provide a means for such optimization. They were derived using the principle that the ionic fluxes in each layer are equal, that is

$$J_{\text{ion}}^{\text{SDC}} = J_{\text{ion}}^{\text{ESB}} \quad (1)$$

where J is current; the subscript refers to ionic defects and the superscript denotes the layer. Moreover, unlike earlier models, our models employ *potential-dependent* instead of *fixed* boundary conditions and a *Poisson* instead of *Laplacian* potential distribution [4].

The predictions of the performance and stability models are shown in Table 1. For an SOFC designed to operate in the full voltage spectrum (i.e., from just beyond¹ *open-circuit* to *short-circuit*) at 500 °C, bilayer electrolytes will remain stable with a maximum thickness ratio ($L_{\text{ESB}}/L_{\text{SDC}}$) of ~ 4 . This value equates to an area-specific resistance (ASR) of $0.11 \, \Omega\text{cm}^2$ for a 10-micron thick electrolyte. However, if the SOFC is designed to operate only up to *maximum power conditions*, then the maximum thickness ratio increases to ~ 140 ($\text{ASR} = 0.05 \, \Omega\text{cm}^2$). Thickness ratio and ASR values are also given for 800 °C in Table 1.

Table 1. $L_{\text{ESB}}/L_{\text{SDC}}$ and ASR ($L = L_{\text{ESB}} + L_{\text{SDC}} = 10 \, \mu\text{m}$) at 800 °C and 500 °C

		$L_{\text{ESB}}/L_{\text{SDC}}$	ASR (Ωcm^2)
800 °C	short circuit	1.0	0.010
	maximum power	7.1	0.003
500 °C	short circuit	4.0	0.11
	maximum power	140	0.05

Next, we report the discovery of a new oxide ion conductor based on Bi_2O_3 doped with Dy_2O_3 and WO_3 (DWSB). Cubic bismuth oxide has the highest oxide ion conductivity known. The conductive cubic phase may be stabilized by doping, and the best of these stabilized bismuth oxides was ESB ($\text{Bi}_{1.8}\text{Er}_{0.2}\text{O}_3$). We have now developed a variant, DWSB ($\text{Bi}_{1.76}\text{Dy}_{0.16}\text{W}_{0.08}\text{O}_3$) with a conductivity of 0.57 S/cm at 800 °C (1.5 times that of ESB) and 0.043 S/cm at 500 °C (2 times that of ESB), shown in Figure 3. The dopants were selected based on a fundamental investigation of polarizability and its effect on structural stability and conductivity [5 - 8]. Hence, we anticipate even better performance than originally predicted when it is incorporated into the bilayer where it should increase the power density, efficiency, and operating temperature range of our low temperature ceria/bismuth oxide bilayer electrolytes.

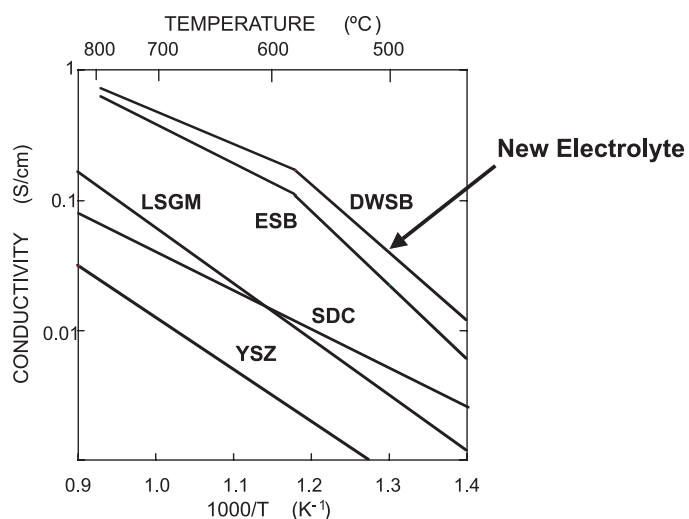


Figure 3. Arrhenius plots comparing the conductivity of various electrolytes.

Finally, we explored various paths for depositing thin and thick films for single layer and bilayer electrolytes before choosing colloidal deposition for its versatility, simplicity, economy and potential for rapid industrial scale-up. With this technique we fabricated an anode (Ni/GDC) supported SOFC with a GDC electrolyte and an $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) cathode. Figure 4 shows an SEM of such a cell. This was done to verify the efficacy of the colloidal deposition technique we had developed, and to compare the performance of our setup with similar ones reported in the literature.

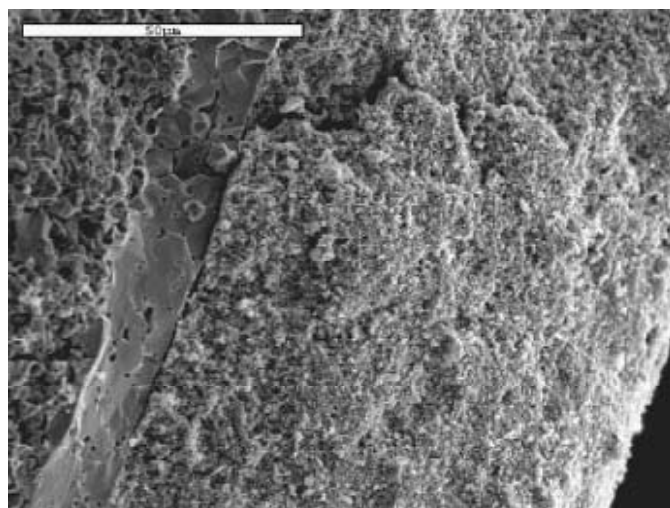


Figure 4. Fractured cross-section of a tested fuel cell: Ni-GDC/GDC (~15mm)/LSCF (~85mm).

Figure 5 shows the current-voltage (I-V) characteristics and power density of the cell, which are comparable to those reported in the literature [9, 10]. In open-circuit conditions, the cell potential decreased with increasing temperature. The shape of the I-V curves became more linear with increasing temperature, possibly due to reduced electrode activation polarization losses at higher temperatures. High OCP and low cell resistance are requisite for high power densities. However, since the OCP and resistance both decrease with increasing temperature, there exists an optimal

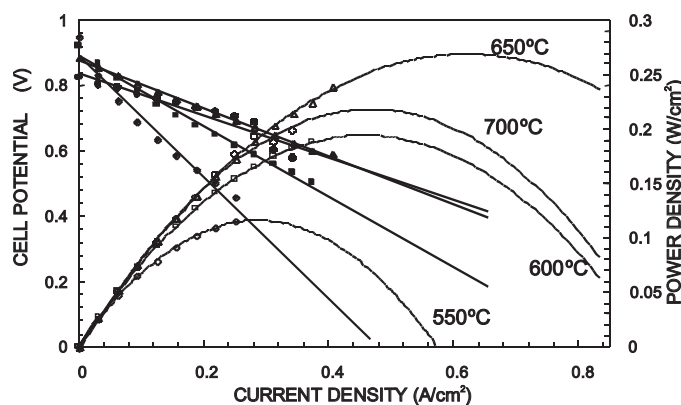


Figure 5. Current-voltage characteristics (closed symbols) and power density (open symbols) of the Ni-GDC/GDC/LSCF SOFC as a function of current density and temperature.

- 1 In open-circuit conditions bismuth oxide requires more protection (i.e., a thicker ceria layer) because of the onset of ambipolar diffusion [4].

temperature where the power density reaches a maximum. Over the I-V range investigated, the cell attained its maximum power density of 0.25 W/cm^2 at 650°C and a current density of 0.6 A/cm^2 . Using our bilayer concept, which adds an electron-blocking ESB layer, will raise the OCP to near theoretical (Nernstian) potential and lower the resistance, resulting in significantly greater power density at this temperature.

Finally, other results, not shown here, indicate that the cathode performance needs improvement. To address this, a variety of cathodes are being developed, such as the composites Ag-ESB and LSCF-ESB, and a relatively new material Bi_2RuO_7 . Early results are promising and show further significant improvements in low-temperature power density are achievable.

Conclusion

The bilayer concept has been confirmed. Ceria/bismuth oxide bilayer electrolytes were shown to be stable and have high performance, even at low temperatures, and thereby have the potential to reduce material and operating costs and increase reliability. The performance and stability of these bilayer electrolytes were shown through theory and experiment, to be functions of the thickness ratio of the constituent layers. We are currently in the process of preparing thin anode-supported SDC/ESB electrolytes by this process.

A reliable and *upscalable* colloidal deposition technique was developed to fabricate the bilayer electrolyte. GDC SOFCs made by this method produced power densities comparable with those found in the literature for similar cells.

Using a sound theoretical basis, a new oxide ion conductor, DWSB, that has the highest known conductivity in the range $400 - 800^\circ\text{C}$ was developed. DWSB, when incorporated in a bilayer (e.g., GDC/DWSB), will produce a highly efficient bilayer capable of high performance, even at low temperatures.

In closing, both experiment and theory support the viability of stable high-conductivity bilayer electrolytes for low temperature solid oxide fuel cells. More work remains to be done regarding optimization of the thickness ratio, which has been modeled but not yet implemented, and the development of high performance cathodes. Nevertheless, present results demonstrate that we are on the right course. That is, by fabricating

thin bilayer electrolytes and developing better cathodes we expect to produce high power density SOFCs at temperatures below 600°C .

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